

UTILIZATION OF PETROLEUM COKES FOR STEAM RAISING

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ABSTRACT

A glut of petroleum coke has made it an attractive source of cheap Btu's, either as a blended fuel or as the primary fuel. Petroleum coke, however, is low in volatiles and contains substantial concentrations of vanadium, nickel, and sulfur, which can be sources of combustion and fireside fouling or corrosion problems if not properly handled. This paper discusses the combustion characteristics of the various types of petroleum cokes used for steam raising and the fireside behavior of the mineral matter they contain.

BACKGROUND

An excess of petroleum coke residues has stirred a great interest in firing all types of petroleum cokes in steam generators used to produce steam and electricity. The residual coke from a crude refining process—considered a residue or byproduct depending upon its utility in the marketplace—is low in volatiles and rich in vanadium, iron and nickel. The low-volatile coke produces a char with a reactivity similar to a bituminous coal. Low-volatile fuels are generally fired in an arch-type furnace to induce ignition and ensure flame stability. Attempts have been made to directly extrapolate the fireside behavior of minerals found in oil to those retained in the coke. However, there is a significant difference in the mechanisms and kinetics of combustion for solid and liquid petroleum products, to significantly alter the behavior of the most troublesome mineral constituents found in the solid fuel. Historically, the corrosion-, slagging-, and fouling-free limit for vanadium in petroleum cokes is several orders of magnitude higher than the trouble-free limit of 50 ppm set for oil.

PETROLEUM COKE

The physical properties and the fuel analysis of a petroleum coke depend upon the crude and the manner in which it was processed. Petroleum cokes—including delayed coke, fluid coke, needle coke, shot coke, and flexicoke—are byproducts of solid residuals from the refining process.

Delayed coking is an endothermic process in which reduced crude is rapidly heated in a furnace batch-wise and then confined to a reaction zone or coke drum under proper conditions of pressure and temperature until the unvaporized portion of the furnace effluent is converted to vapor and coke. Products of the coke are gas, gasoline, gas oil, and coke.

When charging the coke with highly aromatic feedstocks at high pressures (i.e., 100 psig), a coke with a needle-like structure can be produced. The needle coke has high strength and a low coefficient of expansion. It is preferred over sponge coke for use in electrode manufacturing because of its lower electrical resistivity and lower coefficient of thermal expansion.

A third type of coke is produced unintentionally during operating upsets, probably as a result of low coke drum pressures or temperatures, or low API feed gravities. This type of coke is called "shot coke" because it occurs as clusters of shot-size pellets.

Fluid coke, as the name implies, is generated in a fluidized bed reactor operating at 1000°F. Feedstock is sprayed onto a bed of fluidized coke. The thin film of feedstock is vaporized and cracked by steam introduced into the bottom of the reactor as the coke laden with feedstock flows downward and is withdrawn from the bed. The coke is removed from the reactor where it is fed to the fluidized bed burner. Approximately 25 percent of the coke is spent to raise the temperature of the reactor coke back to 1000°F and thus provide for the endothermic losses caused by feedstock vaporization and cracking yields from fluid cokes, which are about 75 to 80 percent that of delayed coke. The resultant fluid coke withdrawn from the burner is a solid, spherical particulate smaller than 8 mesh (i.e., < 2380 μm). The coke is very abrasive and can have a Hardgrove Index as low as 17.

The flexicoke is essentially a fluid coke from a process that includes a gasifier loop for gasifying and heating the coke leaving the fluidized bed burner in the fluid coke system. The fluidized bed burner functions as an intermediate heat exchanger between the reactor and gasifier. Adding the gasifier to the system increases the yield. Flexicoker yields can be 2 to 40 percent that of delayed coker yields. At the higher yields, one might expect higher concentrations of ash. The yields may also be limited by the initial concentration of minerals in the feedstock [1].

Table 1 compares the fuel analysis profiles of the various types of cokes described above. Table 2 compares the mineral composition.

Combustibility of Petroleum Coke

The fuel analysis indicates petroleum cokes are low in moisture and ash; consequently, they have high heating values. Unfortunately, they contain less than 10 percent volatile matter and only a few percent O_2 , making them difficult to ignite. For ignition to occur, the specific rate of heat release from the oxidation process must exceed the rate of heat loss to the unheated char and the environment. Solid fuel particles provide a relatively small surface area for oxidation; and the reactivities of the char, compared with the volatiles released during the initial stage of heating, are low.

To reach a temperature where ignition or self-sustained combustion occurs, the petroleum coke particles depend upon radiant and convective heat exchange from the furnace to compensate for the lack of heat of reaction—otherwise provided by the volatiles. Minimizing excess air during ignition and the initial stages of combustion supports the rise in char temperature required to ignite the petroleum coke. Furnaces and burners designed for low-volatile fuels generally use refractory-lined walls in the immediate vicinity of the burner to support heating the fuel rather than quenching it. They also introduce air stage-wise along the path of combustion, as needed, to minimize the quenching effect of secondary air. As illustrated in Figure 1, an arch-type furnace is used to increase the flame length and provide recirculate heat to stabilize ignition, as shown in Figure 2.

Thermogravimetric analysis (TGA) performed on the various types of petroleum cokes, illustrated in Figure 3, qualitatively shows that there is very little difference in the reactivity of the raw cokes. Char generated by heating the cokes samples at 20°C/min to 1000°C is then reheated under air at a heating rate of 20°C/min. The thermograms appearing in Figure 4 indicate differences in char reactivity are even less once the volatiles have been removed. A comparison of the raw cokes with various rank coals, shown in Figure 5, indicate the reactivity of petroleum coke falls between that of a medium- to low-volatile bituminous and an anthracite. Global kinetic data may be extracted for comparison purposes by applying the Arrhenius equation:

$$\frac{dw}{dt} = K_w W^n = -A W^n e^{R/RT} P_r$$

where, $w = 1$ for a first-order reaction.

All experiments using TGA are performed on a 10-mg sample, 44 μ in size. Although flexicoke appears to be the least reactive of the petroleum cokes, recent field trials have demonstrated that blending of 15-percent flexicoke with a delayed coke resulted in a reduction in carbon loss. It would appear that a reduction in particle size associated with flexicoke can compensate for its slightly reduced reactivity. Generally, the percent carbon in fly ash from a full-scale boiler runs between 20 to 40 percent. This is equivalent to approximately 0.2 to 0.4-percent carbon loss in a coke containing 1-percent ash.

History of Fireside Problems With Heavy Oil Products

The principal ash-forming elements found in crude oil, as given by Bowden, et al., in Table 3 are the same as those found in coal, except for the addition of vanadium, nickel, and zinc [2]. Both inorganic and organic, metallic, oil-soluble forms have been observed for several of the elements. No matter which forms these elements take, the important point to note is they are retained essentially intact during the refining process and are concentrated in the residual oil. Recent X-Ray Absorption Near-Edge Structure (XANES) analysis, performed by the University of Kentucky and illustrated in Figure 6, has shown that vanadyl porphins found in heavy oil also remain intact in during the process of forming petroleum cokes. All the elements listed in Table 3 are intrinsic to the crude. Sodium concentrations may increase considerably if the crude is shipped by sea. However, the sodium level should not exceed 50 ppm in the residual oils if they are properly desalted at the refinery. Asphaltic-base crudes are generally rich in vanadium—particularly those from Venezuela, which often contain more than 500-ppm vanadium, reported as V_2O_5 . Some Middle East crudes, as well as some from California, also contain appreciable amounts of vanadium. Paraffinic-base crudes usually are free of vanadium [3,4]. Refining of the crudes should raise the vanadium levels at least an order of magnitude (i.e., 1000 to 4000 ppm vanadium).

Corrosion and fouling of boilers fired with residual oil are caused by sodium, vanadium, and sulfur in the oil [5-9]. The literature attributes high-temperature corrosion primarily to vanadium, as V_2O_5 in a molten state. Molten V_2O_5 readily dissolves most refractory and metal oxides, exposing virgin metal surfaces to an oxidizing environment. The rate of oxidation is enhanced as the low viscosity and surface tension promote the counterdiffusion of O_2 to the metal surface and corrosion product from the metal surface. Condensation of sodium sulfate lowers the melting temperature of the solution by forming complex vanadates. Thus far, only the complex sodium vanadyl vanadate has been identified in actual deposits. During its formation, free O_2 is released, increasing the corrosion potential at the tube surface. Corrosion is particularly troublesome when the sodium-to-vanadium ratio exceeds 0.3, or the sodium concentration exceeds 20 ppm in the oil. The primary approach

to controlling vanadium corrosion is maintaining surface temperatures below the lowest melting vanadate.

Fouling is caused when the V_2O_5 condenses on fly ash material composed of refractory oxides at temperatures above the melting point of the V_2O_5 . Counter-diffusion of the two components at the particle surface produces a sticky surface, giving the particle a high potential for sticking. Very high concentrations of refractory oxide tend to dry up the V_2O_5 . If the absorption is complete prior to contact with a steam generator surface, fouling is inhibited. If not, severe fouling occurs as a sintered deposit develops on the tube surface. Fouling can also be caused by incomplete combustion, resulting in deposition of soot during operation or poor atomizing during shutdown. Vanadium is retained in oil until the last of the petroleum is vaporized, hence the high concentration of vanadium and sulfur in petroleum cokes. Unspent oil or carbon that deposits on tube surfaces is rich in vanadium and sulfur. Completion of the oxidation of this carbon at the tube surface temporarily raises the melting temperature of the ash, allowing it to melt and react with other ash on the tube surface. On cooling, it solidifies and remains tenaciously attached to the metal surface.

V_2O_3 or V_2O_4 , which have melting points greater than 3500°F , will form in the presence of insufficient excess air [4]. In this case, the vanadium is innocuous and leaves the steam generator as dry ash.

Fireside Behavior of Mineral Matter in Petroleum Cokes

Petroleum cokes containing vanadium in concentrations as high as 4000 ppm have been fired in full-scale steam generators since 1957, free of corrosion or fouling except for occasional deposits attributed to either an excursion in nickel or sodium concentration or operation resulting in total char burnout. The deposits, when formed, consisted of nickel vanadates formed as a result of condensation of a nickel compound and V_2O_5 . Figure 7 illustrates the crystalline nature of the deposit formed. A DTA thermogram on the petroleum coke deposit indicated that two endotherms were encountered upon heating—one coincident with the liquidous line for $V_2O_5 + Ni(VO_3)_2$, and the other coincident with the liquidous line of $Ni_2V_2O_7$ —suggesting the presence of $Ni(VO_3)_2 + Ni_2V_2O_7$.

Combustion tests in a pilot plant of a flexicoke containing 10,000 ppm vanadium, 1700 ppm nickel, 2.35 percent sulfur, and only 5 percent volatiles in a 100-lb/h combustor for 100 hours indicated petroleum cokes with very high vanadium concentrations could be safely burned free of corrosion, slagging, or fouling. Despite the low volatility, ignition was good. The flame was stable, and the carbon loss in the ash ran about 17 percent, representing a 99.2 percent carbon utilization. The material tested came from a storage pile. Because flexicoke is extremely fine, about 60 percent -200 mesh, dirt had been used as a cover or dust suppressant to reduce wind losses. The dirt lowered the vanadium concentration to 50 percent V_2O_5 in the ash and added 31 percent SiO_2 and 11.4 percent CaO . Less than 0.3 percent of the total vanadium actually deposited on the convection bank tubes. Of the vanadium, 75 percent was captured in the fly ash as silicates and calcium vanadates. The remaining 25 percent was unaccounted and included deposited material on other surfaces or loss to the stack. The analysis of deposits appear in Table 4. The 299-g deposit formed took 100 hours to accumulate in a combustor designed to demonstrate fouling within the 5-1/4 hours of testing. Normally, fouling is considered medium if 150 to 300 g forms in 5-1/2 hours, and severe if the weight exceeds 300. Subsequent tests performed on the petroleum coke with the dirt removed indicate some V_2O_5 was formed and deposited on the convection pass probe. Fouling was light and there was no corrosion of carbon steel surfaces restricted to 850°F surface temperatures.

CONCLUSIONS

Formation of vanadium pentoxide during the combustion of vanadium-rich petroleum cokes is inhibited by excess carbon in the fly ash and/or additional mineral species such as SiO_2 or CaO in the ash. Petroleum cokes containing as much as 10,000-ppm V_2O_5 have been fired free of corrosion with minimal fouling.

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Table 1 Fuel Characterization of Petroleum Cokes

Description	Delayed Cokes		Shot Cokes		Fluid Cokes		Flexicokes	
	1	2	1	2	1	2	1	2
Proximate Analysis, wt%								
Fixed Carbon	84.47	80.20	81.35	83.86	89.59	81.50	95.27	84.80
Volatile	8.62	4.48	7.21	9.89	3.07	4.94	1.77	1.28
Ash	1.08	0.72	0.87	0.78	1.05	1.32	2.50	0.99
Moisture	5.95	7.60	0.67	5.69	8.28	2.24	0.46	2.86
Ultimate Analysis, wt%								
Carbon	83.44	81.12	86.81	81.29	92.28	84.41	92.31	92.0
Hydrogen	3.35	3.60	3.48	3.17	1.74	2.12	0.88	0.30
Oxygen	0.04	0.04	0.21	0.93	1.41	0.82	0.04	0.00
Nitrogen	1.71	2.55	2.04	1.60	1.83	2.35	1.52	1.11
Sulfur	4.46	4.37	6.04	5.98	5.32	6.74	2.48	2.74
Ash	1.08	0.72	0.87	0.78	1.05	1.32	2.50	0.99
Moisture	5.95	7.60	0.67	5.69	8.28	2.24	0.46	2.86
HHV, Btu/lb	14,630	14,288	15,121	14,384	13,326	14,017	14,066	13,972

Table 2 Typical Ash Analysis of Various Types of Cokes

Elemental Composition, wt%	Delayed Cokes	Shot Cokes	Fluid Cokes	Flexicokes Production	Flexicokes Stoker Pile
SiO ₂	10.1	13.8	23.6	2.8	28.2
Al ₂ O ₃	6.9	5.9	9.4	1.1	2.9
TiO ₂	0.2	0.3	0.4	0.1	0.6
Fe ₂ O ₃	5.3	4.5	31.6	0.8	2.7
CaO	2.2	3.6	8.9	1.8	10.3
MgO	0.3	0.6	0.4	0.2	0.8
Na ₂ O	1.8	0.4	0.1	2.1	0.5
K ₂ O	0.3	0.3	1.2	0.2	0.0
SO ₃	0.8	1.6	2.0	1.0	10.0
NaCl	12.0	10.2	2.8	8.0	4.5
V ₂ O ₅	56.2	57.0	18.7	79.0	39.9
ASTM Ash Fusion, °F					
Reducing					
I.D.	2810	2617	2513	2196	2222
S.T. (Sph.)	2810	2910	2527	2199	2413
S.T. (Hem.)	2810	2910	2623	2272	2506
F.T.	2810	2910	2685	2322	2800
Oxidizing					
I.D.	2505	2299	2003	2378	2339
S.T. (Sph.)	2597	2605	2111	2454	2528
S.T. (Hem.)	2609	2680	2162	2521	2576
F.T.	2611	2680	2236	2565	2609

Table 1 Principal Ash-Forming Elements in Crude Oil

Element	Type	Solubility in Oil	Probable Chemical Form
Aluminum	Inorganic	Insoluble	Complex aluminosilicates in suspension
Calcium	Organic	Soluble	Not identified
	Inorganic	Insoluble	Calcium minerals in suspension; calcium salts in suspension or dissolved in emulsified water
Iron	Organic	Soluble	Possible iron porphyrin complexes
	Inorganic	Insoluble	Finely sized iron oxides in suspension
Magnesium	Organic	Soluble	Not identified
	Inorganic	Insoluble	Magnesium salts dissolved in emulsified water or in suspension in microcrystalline state
Nickel	Organic	Soluble	Probably porphyrin complexes
Silicon	Inorganic	Insoluble	Complex silicates and sand in suspension
Sodium	Inorganic	Insoluble	Largely sodium chloride dissolved in emulsified water or in suspension in microcrystalline state
Vanadium	Organic	Soluble	Vanadium porphyrin complexes
Zinc	Organic	Soluble	Not identified

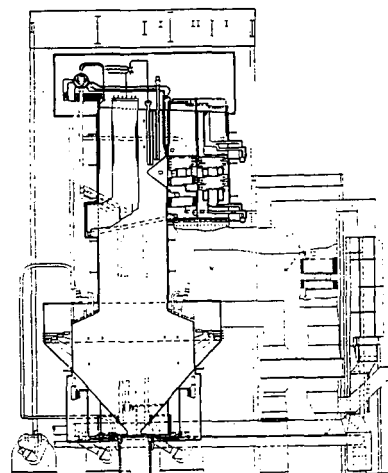


Figure 1 Utility Style Steam Generator Side Elevation

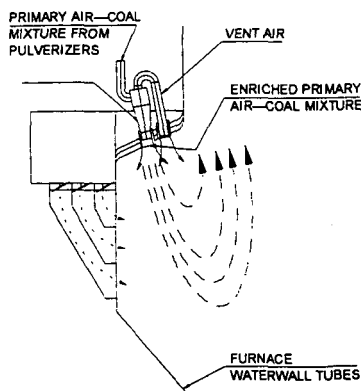


Figure 2 Downshot Cyclone Burner Arrangement

Figure 3 Combustion Profiles of Various Types of Petroleum Cokes

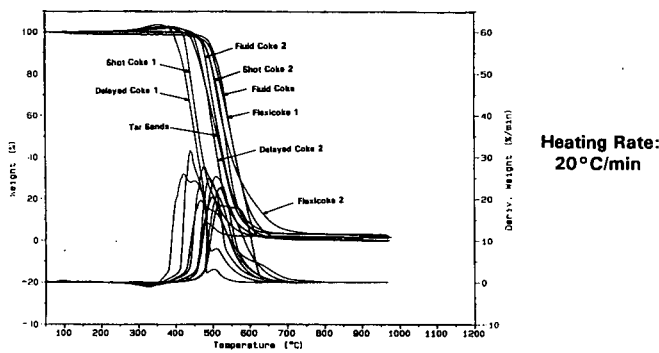


Figure 4 Combustion Profiles of Various Types of Petroleum Cokes Chars

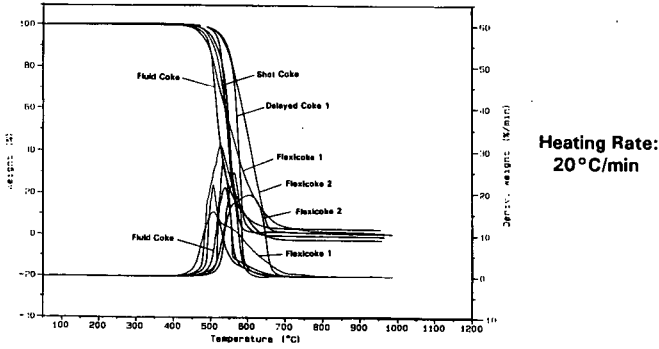
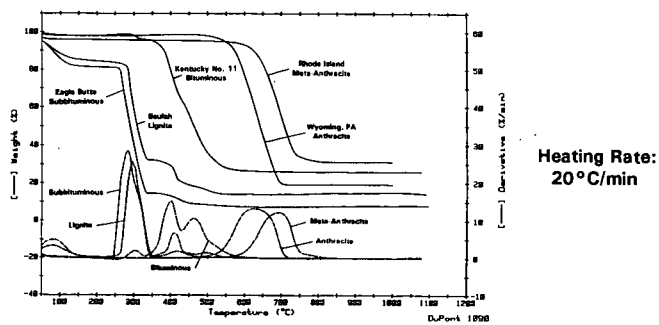


Figure 5 A Comparison of Combustion Profiles of Various Types North American Coals



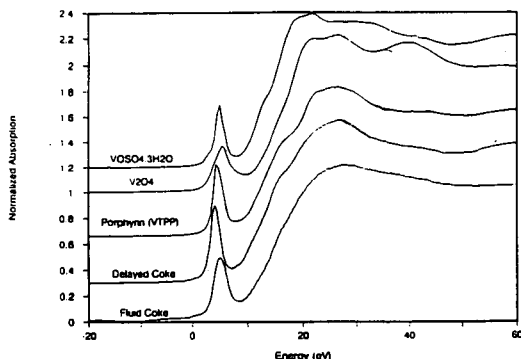


Figure 6 Comparison of the Forms of Vanadium in Delayed and Fluid Coke with the Porphyrins Found in Oil Using X-ray Absorption Near Edge Structure (XANES) Analysis by the University of Kentucky

Deposit Cross Section



Mag. 15X

Pure V_2O_5 Crystals



Mag. 300X

Figure 7 Scanning Electron Microphotography of the Deposit Formed While Firing A Petroleum Coke Whose Ash Contains 85-Percent Vanadium Expressed as V_2O_5

Table 4 Summary of Ash Fouling Probe Test Results

Gas Temperature Entering Probe Bank, °F	2034
Probe Metal Temperature, °F	753
Excess Air, %	20.4
Total Deposit Weight, g (100 hrs)	299
Chemical Composition	wt%
V_2O_5	45.4
NiO	4.8
SiO_2	18.1
Al_2O_3	3.0
Fe_2O_3	2.1
TiO_2	0.6
P_2O_5	1.0
CaO	7.9
MgO	0.3
Na_2O	0.6
K_2O	0.6
SO_3	15.7